Treatment of Dye Intermediate Waste-Water by Fenton and Electro-Fenton Treatments

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Abstract:
In a laboratory study, treatment of real dye-intermediate wastewater having high chemical oxygen demand (COD) in the range of 30,000 to 50,000 mg/L. by fenton and electro-fenton was examined. Batch experiments were conducted to determine optimal operating conditions pH, H_2O_2 dosage, Fe^{+2} dosage and current to obtain the best results. In fenton treatment, the optimal doses of Fe (II) (2%) and H_2O_2 (30%) were 10 ml/L and 20 ml/L. 86% COD removal is obtained by fenton treatment at pH 3. In electro-fenton treatment, the optimal doses of H_2O_2 (30%) was 20 ml/L and current was 2.0 A. 78% COD removal is obtained by electro-fenton treatment at pH 3. These results suggest that, the Fenton process proved to be more efficient for removal of COD from the real dye intermediate wastewater.

Keywords: *Advanced Oxidation Process, COD removal, Dye intermediate waste water, Electro-Fenton, Fenton, H_2O_2*

1. Introduction

The wastewater from dyes and their intermediate manufacturing industry causes serious impact on natural water bodies and land in the surrounding area. High values of COD and BOD, presence of particulate matter and sediments, chemicals which are dark in color leading to turbidity in the effluents causes depletion of dissolved oxygen, which has an adverse effect on the marine ecological system. As dyes are designed to be chemically and photolytically stable, they are highly persistent in natural environments. The improper handling of hazardous chemicals in waste water also has some serious impact on the health and safety of workers putting them into the high-risk bracket for contracting skin diseases like chemical burns, irritation, ulcers, etc. and respiratory problems[1].

The wastewater from dyes and their intermediate manufacturing industry causes serious impact on natural water bodies and land in the surrounding area. High values of COD and BOD, presence of particulate matter and sediments, chemicals which are dark in color leading to turbidity in the effluents causes depletion of dissolved oxygen [3]. Dye intermediate waste water contains high organic loading, due to the high organic load, toxicity or presence of biorecalcitrant compounds, biological processes cannot be used, since no COD removal is achieved biologically. Thus, a biological treatment is not feasible. In these cases, chemical pre treatment can adequately reduce the COD prior to biological treatment [5].

Fenton reagent has been applied to the degradation of a wide range of contaminants, predominantly persistent organic pollutants. The primary benefits of the Fenton reagent are its ability to convert a broad range of pollutants to harmless or biodegradable products, its benign nature (residual reagents do not pose an environmental threat), and the relatively low cost of the reagents. The term Fenton reagent refers to aqueous mixtures of Fe(II) and hydrogen peroxide. The Fenton reagent was first reported by Fenton in 1876[5,8,10]. Although Fenton did not elucidate the mechanism of the reaction named after him, subsequent research has indicated the following net reaction as the predominant process:

$$Fe^{+2} + H_2O \rightarrow Fe^{+3} + HO\cdot + OH^- \quad \cdots\cdots (1)$$

where Fe^{2+} and Fe^{3+} represent the hydrated species, $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ respectively. Reaction (1) is often referred to as the Fenton reaction, although many other reactions occur in Fenton systems.

There are many factors that affect the mechanisms of Fenton-based degradation. Rate constants, hydroxyl radical concentration, pollutant concentration, pH and the presence of other species. Reaction pH for Fenton's oxidation should be in between 2 to 4. Some studies reported an optimum pH of 3 [04, 18, 19]. Studies by [02, 06] gave different optimum pH. Barbusinki et al. reported an optimum pH of between 2.5 to 3 and Homem et al. mentioned a pH of 3.5 to 4.5. Jian-Hui Sun. et al. investigated the degradation of an azo dye Amido black 10B in aqueous solution by Fenton oxidation process. Fenton oxidation of Amido black 10B were 0.50 mM (H_2O_2), 0.025 mM (Fe^{2+}) for 50 mg/L (dye) at an initial pH of 3.50[7]. Mariana Neamtu. Et al.(2003) investigated the degradation of the Disperse Red 354 azo dye in water at laboratory-scale experiments, using four advanced oxidation processes (AOPs): ozonation, Fenton, UV/H_2O_2, and photo-Fenton[12].

This paper reports a study on the treatment of real dye intermediate waste water by two advanced oxidation processes: the Fenton and the electro-Fenton. The aim of this study is to examine in detail the role of a set of selected parameters (pH, temperature, concentrations of Fe(II) and H_2O_2 and current density). Batch experiments were conducted to determine optimal operating conditions for maximum COD removal. $FeSO_4.7H_2O$ is used as the source of Fe(II) in fenton process and Fe(II) is electrically generated from the Electrode (Mild Steel) in electro-Fenton process.

2. Materials and Methods

2.1 Dye Intermediate Waste Water

The untreated wastewater samples were collected from the collection basin of an ETP of a Reactive dye intermediate (J-Acid) manufacturing industry in Ahmedabad, Gujarat. The sampling bottle was cleaned and rinsed carefully with distilled water and then with the effluent. About 2.5 cm air space is left in the bottle to facilitate mixing by shaking. Then samples were stored at 4^0C within one to two hours of sample collection.

2.2 Reagents

Chemicals were used in experiments are $FeSO_4.7H_2O$, H_2O_2, NaOH. Hydrogen peroxide H_2O_2 (30% w/v) solution and hepta hydrated ferrous sulfate ($FeSO_4.7H_2O$) of commercial grade were obtained from M/s Merck (India). NaOH for pH adjustment was also procured from M/s Merck (India). All reagents employed were not subjected to any further treatment. Water used throughout was distilled.

2.3 Experimental Procedure

A sketch of the laboratory reactor (Fenton process) is shown in Figure 1. The experiments were performed in a round-bottomed flask. The reaction solution was stirred with a magnetic stirrer using a constant speed to maintain a well-mixed solution during the experiments. In every assay, a 500 ml sample was placed into 1000 ml flask. In every case, the reaction was started by adding the dose of H_2O_2 and $FeSO_4.7H_2O$. All experiments were carried out in batch mode. Several set of experiments were carried out to determine the range of hydrogen peroxide and iron needed to obtain optimum results. Oxidation experiments were performed with varying the reaction time. Then samples were withdrawn from the circulation tank at time intervals of 5, 10, 15, 20 and 25 minutes for the COD analysis.

A sketch of the laboratory reactor (Electro-Fenton process) is shown in Figure 2.The experiments were performed in a round-bottomed flask. The reaction solution was stirred with a magnetic stirrer using a constant speed to maintain a well-mixed solution during the experiments. Electrodes used are of MS-MS. These electrodes are connected with DC power supply in every assay; a 500 ml sample was placed into 1000 ml flask. H_2O_2 (30%) is added in the sample. Then samples were withdrawn from the circulation tank at time intervals of 5, 10, 15, 20 and 25 minutes for the COD analysis for different current densities.

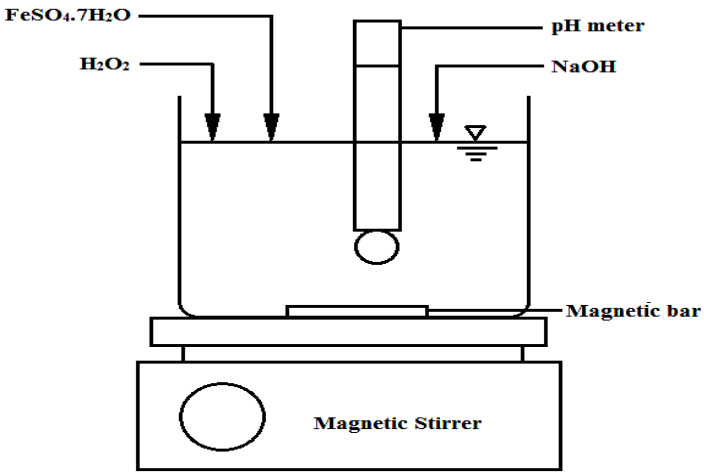

Figure 1 Fenton Process

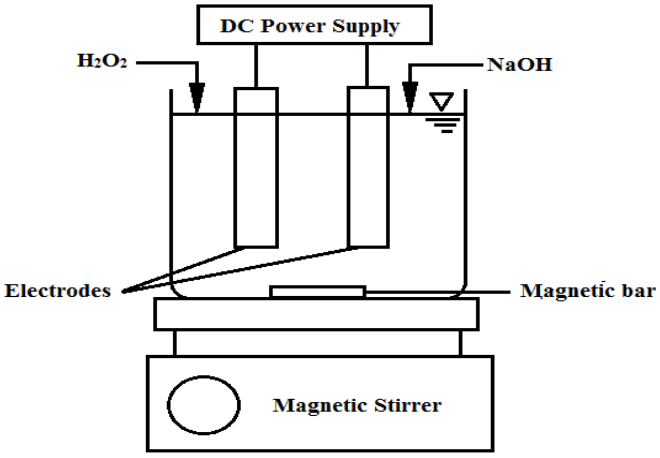

Figure 2 Electro-Fenton Process

2.4 Sample Analysis

pH of the sample is adjusted by using NaOH and measured by pH meter is of make EI products, Parwanoo (H.P), India. pH meter is calibrated by using commercially available Thallate buffer. Waste water sample is mixed with the help of Magnetic Stirrer of make Remi Scientific Instruments ltd., Mumbai, India. Waste water sample is mixed with the help of Magnetic Stirrer from the company Remi Scientific Instruments ltd., Mumbai, India. Raw and treated waste water sample is analyzed for COD according to the methods summarized in the standard methods for the analysis of wastewater [21].

3. Results and Discussion

The wastewater characteristics play a significant role on its treatment. Raw wastewater parameters were measured and listed in Table 1. These results indicate that this wastewater contains high load of organic and inorganic matter. Therefore, this wastewater can cause serious damage to the environment when discharged directly without proper treatment.

Table 1 Ranges of Characteristics of Raw Waste Water

SR. NO.	CHARACTERISTICS	VALUES
1	Chemical Oxygen Demand (COD)	34560-46400 (mg/l)
2	pH	0.8 - 1.5

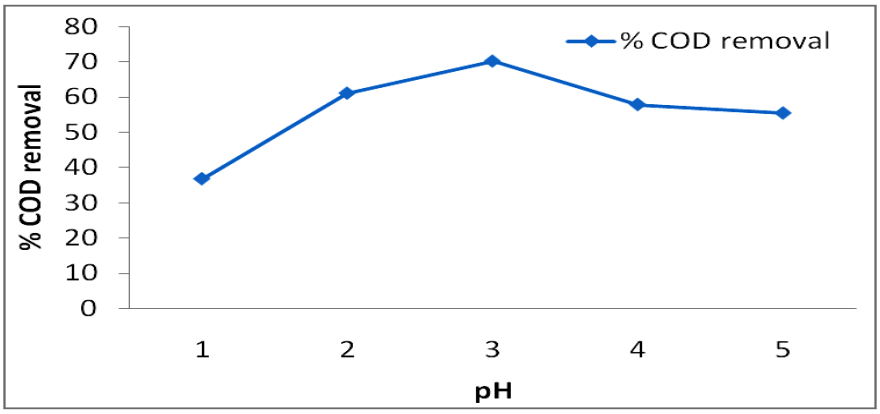

Figure 3 Effect of pH

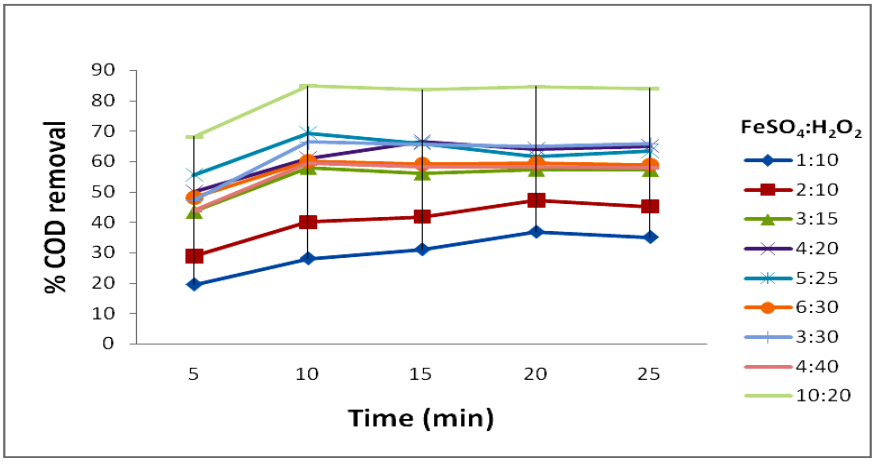

Figure 4 Effect of Reactive Time

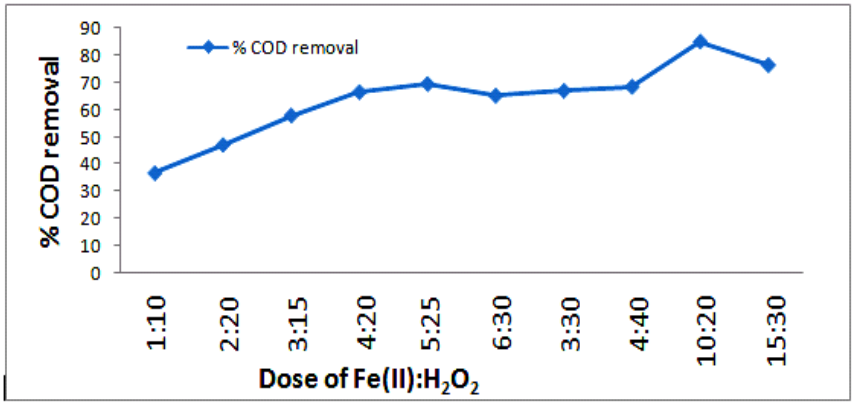

Figure 5 Effect of Dose

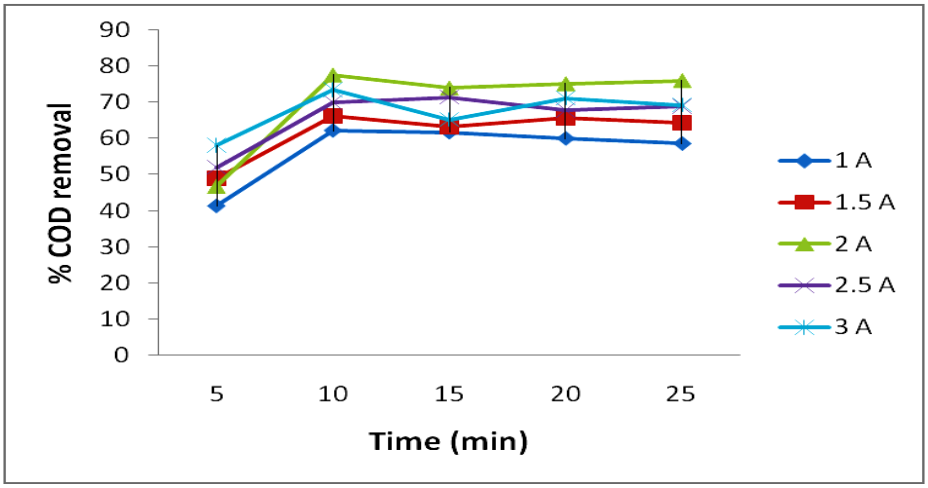

Figure 6 Effect of Current Supplied

In this study, pH 2.5 is the optimum pH. The effect of pH on the COD removal as shown in Figure 3, was investigated with dose of 2 ml of $FeSO_4.7H_2O$(2%) : 25 ml of H_2O_2(30%) and operating time at 10 minutes. Maximum COD removal of around 70 % is achieved at pH 3. Optimum pH for maximum % COD removal of dye intermediate waste water is considered as 3.

The effect of time was studied at the different dose of fenton's reagent. Figure 4 illustrates the removal of COD as a function of operating time. It is clearly seen from Figure 4 that, the operating time has a significant effect on the pollutant removal. When the operating time changed from 05 to 25 minutes, maximum COD removal efficiency of around 86% was obtained at 10 minutes.

Optimum dose of fenton's reagent has been studied by varying different ratio of $FeSO_4.7H_2O$(2%):H_2O_2(30%). As shown in Figure 5, different doses of fenton's reagent have been studied for maximum COD removal of dye intermediate waste water by keeping pH at 3 and reactive time of 10 minutes. Optimum dose of $FeSO_4.7H_2O$(2%):H_2O_2(30%) for maximum COD removal of around 86% is 10(ml/l):20(ml/l).

In Electro-Fenton treatment, series of experiments carried out at pH 3. Dose of H_2O_2 (30%) and surface area of the electrode kept constant at 20 ml/L and 25 cm^2. Current supply varies from 1-3 A. Figure 6 shows that the maximum COD removal of 78% is achieved at 2 A.

4. Conclusion

The degradation of wastewater from dye intermediate manufacturing industry was investigated by the Fenton, Electro-Fenton processes. The COD removal efficiency was strongly affected by many factors such as the concentration of H_2O_2, Fe^{+2} and the ratio of organic materials to the Fenton reagents.

The optimum operating conditions of the Fenton oxidation process involve 20 mL H_2O_2 (30%), 10 mL Fe^{+2}(2%), 21000 mg l-1 initial COD and 20 min of treatment time. Under these conditions, the COD removal efficiency was observed to be 86 %.

The optimum operating conditions for the Electro Fenton oxidation of wastewater was carried out at the given operating conditions (pH 3, H_2O_2 (30%): 20 ml/L, Reactive time : 10 minutes, Current density: 60 mA/cm^2) which produced a COD removal of 78%.

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